Spectroscopic Study of REMPI for Rotational Temperature Measurement in Highly Rarefied Gas Flows

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Abstract. A measurement technique of thermodynamic variables with high sensitivity is strongly demanded for analyses of highly rarefied gas flows. REMPI (Resonantly Enhanced Multiphoton Ionization) is a powerful optical tool because of its high sensitivity even in highly rarefied gas flows and ability to measure nonequilibrium among internal (translational, vibrational, and rotational) energy. In this study, to investigate fundamental properties of REMPI signal, the experimental apparatus of 2R+2 N_2-REMPI is constructed and the REMPI spectra are measured along the center line of a free molecular jet. A method of Boltzmann plot using the spectral lines of both O and P branches is proposed, determining electronic transition dipole moments in Hönl-London factors experimentally from the relative line strength of O and P branches. Then an effect of an experimental noise on a rotational temperature measured by the Boltzmann plot becomes smaller because the number of the lines used for the plot increases. By using the factors, simulated spectra agree well with experimental ones, suggesting feasibility of rotational temperature measurement by a spectral fitting.

INTRODUCTION

Nowadays, analyses of highly rarefied gas flows are strongly demanded, related to vacuum science and aerospace engineering. For example, to diagnose material surfaces for ultra-high vacuum devices, we have to examine not only static properties such as amount of gas molecules desorbed from solid surfaces, but also dynamic properties of gas molecules interacting with these surfaces, such as energy transport processes. In the space engineering, impingement of exhaust gas jets from satellite thrusters on the solar battery panels or antennae is also a serious problem including interaction of very cooled gas molecules with these surfaces and contamination of the exhaust gas molecules.

So far, mass spectrometers and Patterson probes have been used to measure number density of rarefied gas flows, but these method cannot measure nonequilibrium among internal (translational, vibrational, and rotational) energy. This means that the molecular energy transport processes between gas molecules and solid surfaces cannot be examined precisely. On the other hand, spectroscopic methods such as electron beam fluorescence (EBF) [1] and laser induced fluorescence (LIF) [2] have enabled to detect the nonequilibrium in rarefied gas flows, because they are based on internal energy distributions of gas molecules. However, even LIF, which is the most sensitive method among the conventional spectroscopic methods, can hardly be applied to the rarefied gas flow below 10^{12}molecules/cm^3 [1], because these techniques are based not on the detection of molecules themselves, but on the detection of fluorescence or scattering light emitted from molecules.

For non-intrusive measurement with high sensitivity, a REMPI (Resonantly Enhanced Multiphoton Ionization) technique is the most suitable for measurement of thermodynamic variables of highly rarefied gas flows. In the REMPI technique, ions excited to the ionization state from the ground state by multiple photons are detected as a signal and its spectra depending on the wavelength of laser beam are analysed to measure temperature. In the case of N_2, the detection limit of 10^9molecules/cm^3 for 2R+2 REMPI [3], and 10^5molecules/cm^3 for 2R+1 REMPI [4] have been reported.

To estimate rotational temperatures of free molecular flows by REMPI spectra, we have investigated the dependence of 2R+2 N_2-REMPI spectra on temperature by the simulation of the spectra, and we proposed

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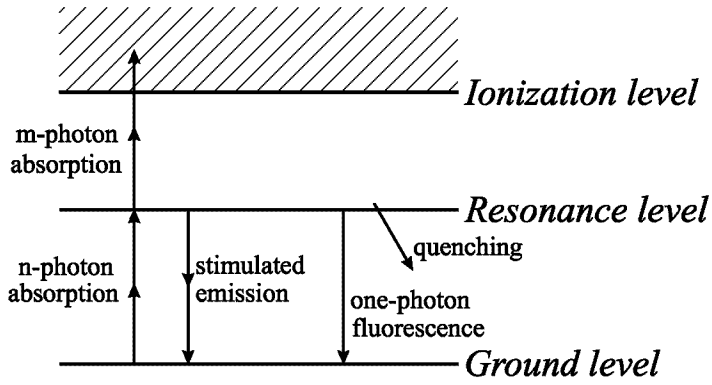

FIGURE 1. Modeling of nR+m REMPI process

appropriate spectral lines for the Boltzmann plot to measure rotational temperature accurately [5]. From this result, for relatively high temperature (> 100 K) it is found that Boltzmann plot using spectral lines of O branch is suitable for a measurement of rotational temperature. In this method only spectral lines of one branch can be used, because it is difficult to determine the transition dipole moments in the rotational transition strength (two-photon Hönl-London factor) theoretically. However, since the number of the lines for the Boltzmann plot is limited, the measured temperature will be easily affected by an experimental noise. In this study, therefore, we determine the transition dipole moments of O and P branches experimentally from the REMPI spectra. Then the Boltzmann plot using the lines of both O and P branch becomes feasible, and the influence of the noise on the measured temperature becomes smaller as an increase in the number of the lines. Moreover, measurement of rotational temperature by the spectral fitting method becomes possible. If using this method, we can use the spectral lines that cannot be used because of the overlap of the lines.

THEORY OF REMPI

Fundamental Principles

Fundamental principles of REMPI were described in the previous paper [5]. Here we summarize them.

Figure 1 shows the process of nR+m REMPI. Molecules are excited to the resonance state by n photons, then they are ionized by m photons. In general, photoionization of gas molecules using multiple photons has very low transition probability. Using REMPI method, however, high transition probability can be established because gas molecules pass through the resonance state before ionization. Because REMPI spectra depend strongly on the transition process from the ground state to the resonance state, the rotational energy distribution can be measured using the REMPI spectra.

In this study, nitrogen is used as carrier gas to examine the fundamental properties of REMPI, because it is the main constituent of air and one of the main constituent of exhaust gas components for satellite thrusters [6]. For N_2-REMPI, 2R+2 and 2R+1 schemes have been widely employed for analyses of rotational energy distribution of N_2. The latter has the advantages of high sensitivity, easy assignment of the spectra, and possibility of the direct analysis of the rotational energy distribution, in comparison with the former. However, it needs a laser source whose wavelength is around 200nm, thus a complicated optical system including a frequency tripled dye laser has to be provided. Further, the intensity of the laser beam will decrease because of the absorption by O_2 molecules in air. In this study, therefore, we employ 2R+2 N_2-REMPI because of its easy optical arrangement and no consideration of O_2-absorption.

REMPI Spectra

Assuming the laser power to be constant, the rotational line intensity in 2R+2 N_2-REMPI spectra is given by [3]

$$I_{J',J''} = Cg(J'')S(J',J'')\exp(-E_{rot}/kT_{rot}), \tag{1}$$

where C is the constant independent of the rotational quantum number of the ground and the resonance state (J'' and J', respectively) including laser flux, number density, vibrational transition strength (Franck-Condon factor) and so on. $g(J'')$ is the nuclear spin degeneracy depending on the parity of J'' and the species of the molecule. For N_2, $g(J'')$ takes 3 and 6 for odd and even J'', respectively. $S(J', J'')$ is the rotational transition strength (two-photon Hönl-London factor), which depends on the electronic angular momentum about the internuclear axis and on the polarization of input light. k is the Boltzmann's constant, T_{rot} the rotational temperature, and E_{rot} the rotational energy. Plotting $\ln(I/gS)$ versus E_{rot}/k according to the above equation, rotational temperatures can be easily derived from its slope $-{T_{rot}}^{-1}$ (Boltzmann plot).

TABLE 1. Two-photon Hönl-London factors of N_2 for the $a^1\Pi_g \leftarrow X^1\Sigma_g^+$ transition using linearly polarized light [7]

Branch	$S(J', J'')$
O $(\Delta J = -2)$	$M(O)J''(J''-2)/15(2J''-1)$
P $(\Delta J = -1)$	$M(P)(J''+1)/30$
Q $(\Delta J = 0)$	$M(Q)(2J''+1)/10(2J''-1)(2J''+3)$
R $(\Delta J = 1)$	$M(R)J''/30$
S $(\Delta J = 2)$	$M(S)(J''+1)(J''+3)/15(2J''+3)$

The two-photon Hönl-London factors for the $a^1\Pi_g \leftarrow X^1\Sigma_g^+$ transition are shown in Table 1 [7]. The $M(O)$–$M(S)$ are the transition dipole factors given by products of the electronic dipole transition moments, and they depend on the kind of the branches. Generally, it is difficult to determine the transition dipole moments theoretically for multiphoton transitions such as REMPI. However, since they are independent of J, they can be considered as constants [7] when the spectral lines of REMPI in the same branch (for example, only O branch) are analysed. On the other hand, if the values of M are determinined experimentally, the Boltzmann plot using multiple branches (for example, both O and P branches) becomes feasible.

EXPERIMENTAL APPARATUS

Figure 2 shows the experimental apparatus that we constructed for measurments of REMPI spectra of a free molecular flow.

Nitrogen gas is issued via a sonic nozzle, whose diameter D is 0.50mm, into a vacuum chamber. The chamber is evacuated by two turbo molecular pumps. For the stagnation pressure of 0.60Torr (80Pa) and the temperature of 294K, the pressure in the chamber is kept at 3.3×10^{-5}Torr (4.4×10^{-3}Pa).

We use Nd–YAG pumped dye laser (Spectra–Physics, DCR–3D(10) and PDL–2) with Rhodamine 6G dye as the laser source, and the output is frequency-doubled by a BBO crystal. The energy, oscillation frequency, and duration time of the laser is 11.3mJ/pulse, 10Hz, and 7ns, respectively. The light is focused by a quartz lens (f = 120mm) into the free molecular flow of nitrogen. The focal point is 5mm downstream from the nozzle exit along the center line. The ionized molecules at the focal point are detected by a secondary electron multiplier (Murata, CERATRON®). The ion signal is amplified by a current-input preamplifier and averaged by a boxcar integrator, and the intensity of the signal is stored to a personal computer. To collect the ions by the detector effectively, an anode plate (repeller) and two cathode plates with a hole (ϕ = 10mm), which act as "lenses" for electric field, are placed in front of the detector as shown in Fig. 3.

The signal intensity is integrated 128 times for each wavelength, and the wavelength step of the scanning is 0.001nm.

RESULTS AND DISCUSSION

REMPI Spectra and Boltzmann Plot

As mentioned in the previous paper [5], for relatively high temperature (> 100 K) Boltzmann plot using O branch is suitable for a measurement of rotational temperature. Around 300 K, P branch is also suitable.

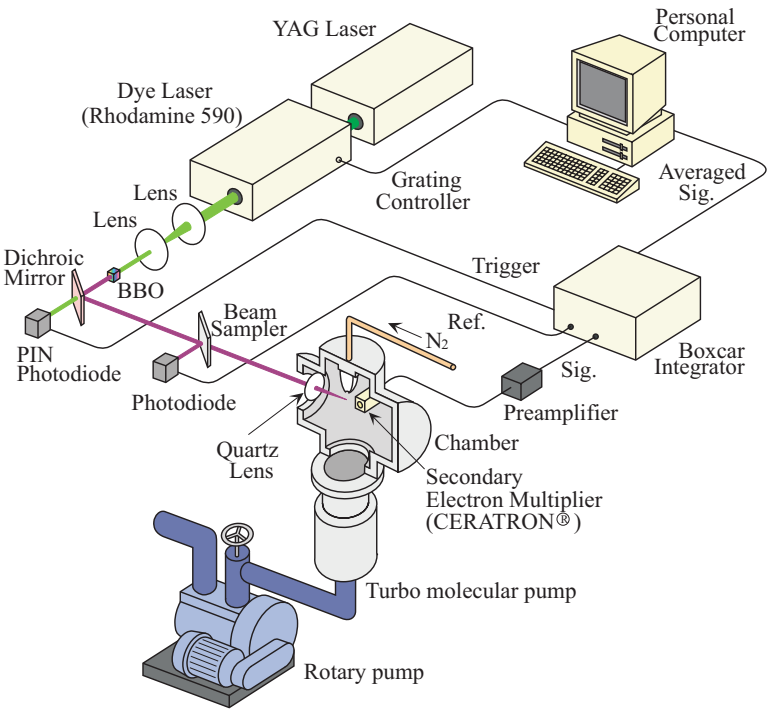

FIGURE 2. Experimental apparatus

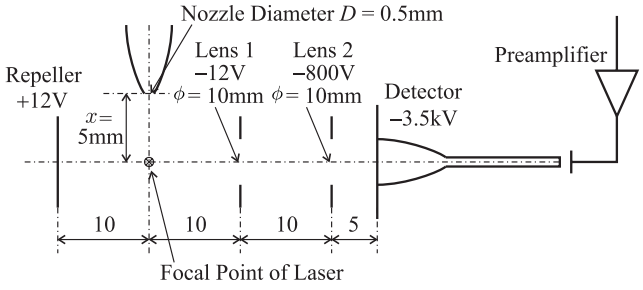

FIGURE 3. Detector system

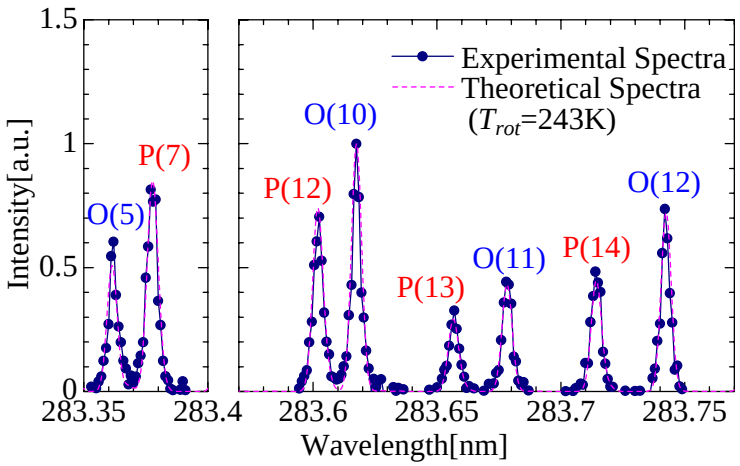

FIGURE 4. Experimental and simulated REMPI spectra

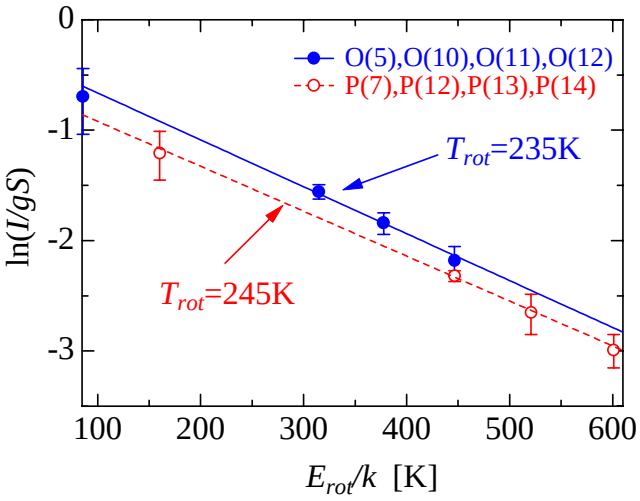

FIGURE 5. Boltzmann plot using O or P branch

Figure 4 shows the REMPI spectrum measured experimentally using the apparatus described in the previous chapter. The stagnation pressure and temperature are 0.60Torr and 294K, respectively. In this case, the number density at the focal point becomes $1.6\times10^{13}/\mathrm{cm}^3$. In this figure, the closed circles and the solid line indicate the experimental spectrum, and the broken line indicates the simulated one (see below). Because the spectral lines existing from 283.4nm to 283.57nm are crowded and cannot be separated each other, these lines can hardly be used for the Boltzmann plot. Therefore we did not measure the spectrum in this region.

Figure 5 shows the Boltzmann plot using the REMPI spectra depicted in Fig. 4. In this figure, the horizontal axis indicates E_{rot}/k and the vertical one $\ln(I/gS)$. The closed circles correspond to O(5), O(10), O(11), and O(12), and the open circles to P(7), P(12), P(13), and P(14). The solid and broken lines indicate the least-square fitting for O and P branches, respectively. For the Boltzmann plot of this figure, $M(O)$ and $M(P)$ are assumed to be 1. This assumption does not affect the slope of the lines, thus the deduced rotational temperature. The slopes of the lines are determined as $(4.25 \pm 0.85) \times 10^{-3}\mathrm{K}^{-1}$ and $(4.07 \pm 0.56) \times 10^{-3}\mathrm{K}^{-1}$ for O and P branches, respectively. From this result the rotational temperature is deduced as 235^{+59}_{-39}K for O branch and 245^{+40}_{-30}K for P branch, showing that temperatures deduced from the Boltzmann plot using O and P branch are almost the same.

Sensitivity

We examined the dependence of the REMPI signal intensity on number density and the detection sensitivity of our experimental apparatus. Figure 6 shows the dependence of the line intensity of O(10) and P(12) lines on the number density at the focal point. From this figure, it is certain that the intensity of the REMPI signal depends linearly on the number density.

Figure 7 and 8 shows the REMPI spectra for the number density of $1.6\times10^{13}/\mathrm{cm}^3$, $5.3\times10^{12}/\mathrm{cm}^3$, and $4.0\times10^{12}/\mathrm{cm}^3$. In these figures, the signal intensity is normalized by the intensity of O(10) line for $1.6\times10^{13}/\mathrm{cm}^3$. From Fig. 8, the S/N is considered to be about 1 for $4.0\times10^{12}/\mathrm{cm}^3$. Therefore, the detection sensitivity (the limit of measurement) of our apparatus is determined as 4×10^{12}molecules/cm^3.

To increase the sensitivity, the laser flux and the gain of the secondary electron multiplier (SEM) can be increased. When we increased the gain of the SEM, however, the level of the background noise became higher, and the S/N became relatively lower. Therefore, to increase the S/N, the effect of the background noise should be decreased by removing the causes of the noise.

One of the sources of the background noise seems to be the pump oil vapor ionized by the laser beam, which is emitted from the rotary pump used as a backing pump of the turbo molecular pump. To decrease the effect, dry pump can be used as a backing pump. Instead, since oil molecules are far heavier than nitrogen, we can

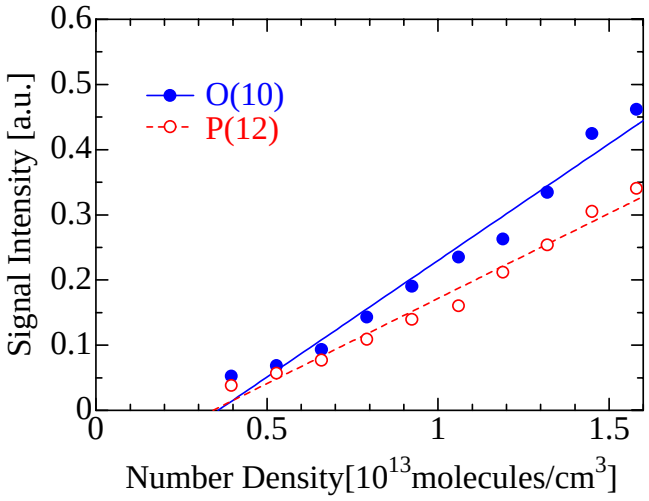

FIGURE 6. Dependence of REMPI signal intensity on number density

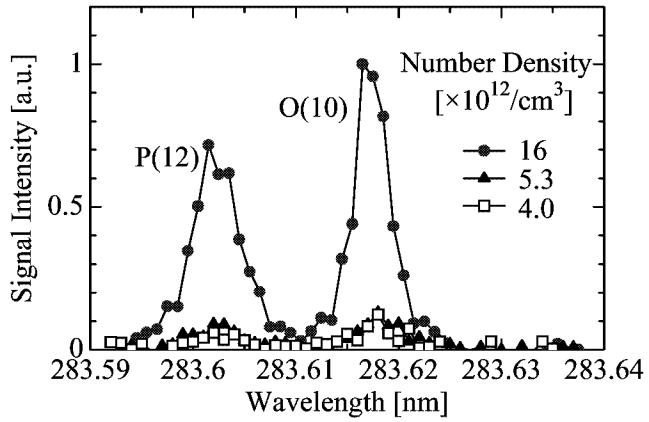

FIGURE 7. Dependence of REMPI spectra on number density

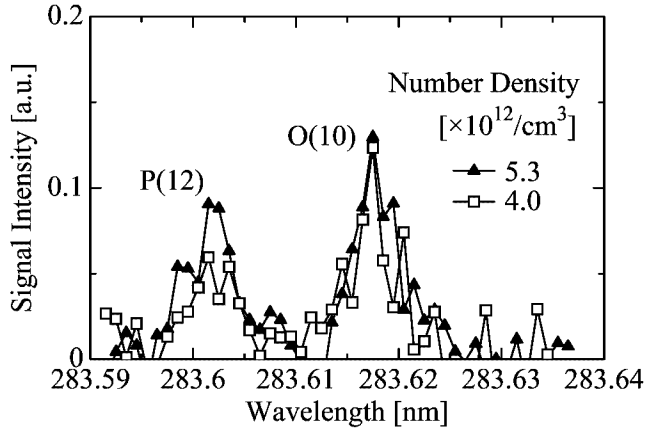

FIGURE 8. REMPI spectra at low number density

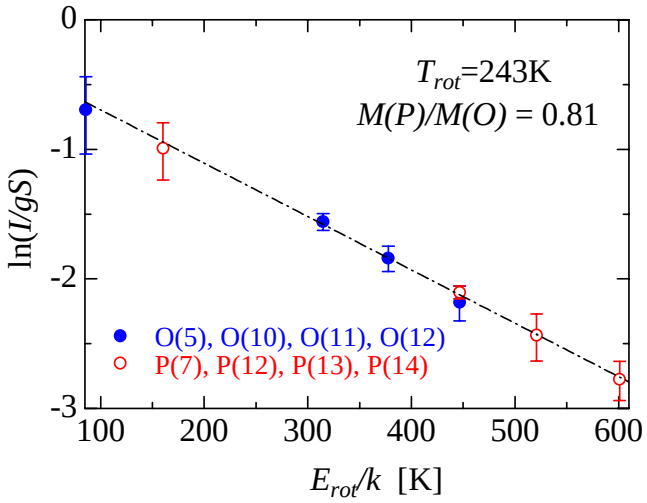

FIGURE 9. Boltzmann plot using both O and P branches

separate the noise from the signal using the time-of-flight mass spectrometry (TOF-MS). To use the method, however, the distance from the focal point to the detector has to be longer, and then the efficiency of ion detection may be decreased.

Another source of the background noise seems to be the ion feedback at the SEM. Since the background pressure is high and there are neutral molecules in the SEM, they are ionized by electrons accelerated by the electric field in the SEM. To decrease the effect, the background pressure at the SEM should be sufficiently low. To let the background pressure be lower, pumps with high throughput should be used. Moreover, it may be effective to improve the apparatus by dividing the detector chamber from the main chamber, and pumping differentially to let the background pressure of the former be lower than that of the latter.

Boltzmann Plot using O and P Branches

For the Boltzmann plot using one branch, the uncertainty of the slope is relatively large, and it results in large uncertainty of the deduced temperature. It is because the number of the spectral lines is limited.

In Fig. 5, the interval of the two lines in the vertical direction corresponds to $\ln\left[M(P)/M(O)\right]$. If we can determine $M(P)/M(O)$ experimentally using the spectra, the Boltzmann plot using both O and P branch becomes possible. As a result, we determined that $M(P)/M(O) = 0.81$. Using this value, the slope of the line for the Boltzmann plot using O(5), O(10), O(11), O(12), P(7), P(12), P(13), and P(14) lines is deduced as $(4.12 \pm 0.36) \times 10^{-3}\mathrm{K}^{-1}$, and the rotational temperature as 243^{+23}_{-20}K (shown in Fig. 9). In this method, the standard deviation of the slope ($0.36 \times 10^{-3}\mathrm{K}^{-1}$) becomes smaller than those of the slope for the conventional method of the Boltzmann plot using one branch ($0.85 \times 10^{-3}\mathrm{K}^{-1}$ and $0.56 \times 10^{-3}\mathrm{K}^{-1}$ for O and P branches, respectively).

Then we simulated the spectrum using Eq. (1) with $M(P)/M(O) = 0.81$ at $T_{rot} = 243$K and compared it with the experimental one. Effects of line broadening and laser linewidth are taken into account for the simulation [5,8]. The simulated spectrum is shown by the broken line in Fig. 4, and it is found that the simulated spectrum agrees well with the experimental one. From this result, it is clear that the value of $M(P)/M(O) = 0.81$ and the deduced rotational temperature $T_{rot} = 243$K are reasonable, and the Boltzmann plot using lines of both O and P branches is feasible. Moreover, it is found that, using the $M(P)/M(O)$ value, measurement of the rotational temperature by searching the simulated spectrum fitting best to the experimental one (fitting method) becomes possible.

CONCLUSION

In this study, we constructed the experimental apparatus for REMPI and we measured the REMPI spectra on the center line of the free molecular flow to determine the rotational temperature. Following concluding remarks are obtained.

1. From the REMPI spectra, for relatively high temperature near 300K rotational temperature can be measured by the Boltzmann plot using spectral lines of either O or P branch. For example, when the stagnation pressure and temperature are 0.60Torr and 294K, the rotational temperarute at $x/D = 10$ of the free molecular flow is found to be 235K or 245K by O or P branch, respectively.

2. The detection sensitivity of our apparatus is 4×10^{12}molecules/cm^3. To increase the sensitivity, the effect of noise should be decreased by improving the experimental apparatus such as pump system. Moreover, it is effective to divide the detector chamber from the main chamber and use the differential pumping system.

3. To let the Boltzmann plot using lines of both O and P branches feasible, we determined the value of $M(P)/M(O)$ experimentally, and it is found to be 0.81. From the Boltzmann plot using both O and P branches and $M(P)/M(O) = 0.81$, on the above-mentioned condition the rotational temperature is found to be 243K. For this method of the plot, the uncertainty of the deduced temperature, i.e. the effect of experimental error, becomes smaller.

4. When the experimental spectrum is compared with the simulated one using $T_{rot} = 243$K and $M(P)/M(O) = 0.81$, they agree well with each other. From this result, it is found that the value of $M(P)/M(O) = 0.81$ and the deduced rotational temperature $T_{rot} = 243$K are correct, and the Boltzmann plot using lines in both O and P branches is feasible. Moreover, if using the value of $M(P)/M(O)$, measurement of the rotational temperature by the spectral fitting method becomes possible.

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REFERENCES

1. Dankert, C., Cattolica, R., and Sellers, W., "Local measurement of temperatures and concentrations: A review for hypersonic flows" , in New Trends in Instrumentation for Hypersonic Research, 1994, pp. 563–581.
2. Niimi, T., Fujimoto, T., and Shimizu, N., Opt. Lett., 15–16, 918–920 (1990).
3. Carleton, K. L., Welge, K. H., and Leone, S. R., Chem. Phys. Lett., 115(6), 492–495 (1985).
4. Lykke, K. R., and Kay, B. D., J. Chem. Phys., 95(4), 2252–2258 (1991).
5. Mori, H., Ishida, T., Hayashi, S., and Niimi, T., "Fundamental Study of REMPI as a Measurement Technique for Rarefied Gas Flow" , in RAREFIED GAS DYNAMICS, vol. 1, CÉPADUÈS ÉDITIONS, 21st International Symposium on Rarefied Gas Dynamics, Marseille, 1999, pp. 575–582.
6. Dettleff, G., Progress in Aerospace Sciences, 28, 1–71 (1991).
7. Halpern, J. B., Zacharias, H., and Wallenstein, R., J. Mol. Spectrosc., 79, 1–30 (1980).
8. Mori, H., Ishida, T., Hayashi, S., Aoki, Y., and Niimi, T., JSME International Journal, Series B1, 43 (2000), to be published.